The Possibilities of Reusing the Ceramic Carriers Coming from Used Auto Catalytic Converters

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Abstract

The application of automobile catalytic converter has significantly helped to reduce air pollution of the exhaust gas released to the atmosphere. The main aim of auto catalytic converter installed in a car is to reduce the carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxide (NO_x) emissions below the legislated levels. They are converted into harmless nitrogen, carbon dioxide and water. These catalytic converters responsible for the catalytic function contain precious metals such as platinum, palladium and rhodium. Catalytic converter is built based on metallic or ceramic carrier with porous structure of honeycomb shape, covered by the layer of PGM metals (Platinum Group Metals). Such construction increases the active surface which is the contact zone of precious metals with fumes. Catalytic carrier is wrapped by fibrous material and closed to stainless steel shell. As the lifetime of catalytic converters is limited; converters should be periodically maintained and after some working time, updated. Therefore, more and more used auto catalytic converters (both from exchanged and exploited cars) are placed on the scrap disposal sites. Due to high value of materials used in catalytic converters and necessity of waste management, there is an increasing interest in their recovery from waste (not only metallic part but concurrently ceramic part) to ensure the profitability of this process. The paper presents possibility of reusing ceramic parts e.g. in obtaining alumina which is important in Bayer`s method.

Keywords

Used Auto Catalytic Converters; Platinum Group Metals; Ceramic Carrier

Introduction

Quick development of industry and civilization progress causes the essential threat to the human natural environment. So, currently the most important problem is environmental protection. The utilization of gaseous pollution emitted to the atmosphere is one of its aspects. Automobile industry and industrial establishments seem to be the main source of that kind of pollution.

The emission of gaseous pollution to the atmosphere can be reduced in two ways: the first one includes the appropriate choice of raw materials and their adequate preparation during the design process. The second way is used when the whole reduction of gaseous emission during the technological process is impossible, therefore the waste gases are cleaned (Online2).

In order to reduce exhaust gases from cars, which significantly polluted air, application of auto catalytic converters is very helpful. At present every new car must be equipped with a catalytic converter, in which the precious metals such as platinum, palladium and rhodium play a catalytic role.

As the lifetime of catalytic converters is limited; converters should be periodically maintained and after some working time, updated. Therefore, more and more used auto catalytic converters (both from exchanged and exploited cars) are placed on the scrap disposal sites. These used catalytic converters were discarded on landfills in the past. Today environmental pollution of air, soil and ocean contaminated by this kind of waste has become a serious problem. Due to high value of materials used in catalytic converters and necessity of waste management, there is an increasing interest in their recovery from waste to ensure the profitability of this process. Finally, the recovery of precious and other metals is beneficial because it limits both the amount of disposed waste and energy consumption, as well as reserves the natural resources. Additionally, pollution emitted during the recovery of metals from waste is

lower than that emitted during their production from primary raw materials. Recovery of Platinum Group Metals (PGM) from used catalytic converters has slightly increased in the last ten years, but still not sufficient (Fornalczyk, LMPC 2009). What is more, the problem of ceramic parts obtained after PGM metals recovery still remains.

The Auto Catalytic Converters

The main aim of auto catalytic converter installed in a car is to reduce the carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxide (NO_x) emissions below the legislated levels. They are converted into harmless nitrogen, carbon dioxide and water. Catalytic converters responsible for the catalytic function contain precious metals such as platinum, palladium and rhodium.

Catalytic converter (see Figure 1) is built based on metallic or ceramic carrier with porous structure of honeycomb shape, covered by the PGM metals layer. Such construction increases the active surface which is the contact zone of precious metals with fumes. Catalytic carrier is wrapped by fibrous material and closed to stainless steel shell [Fornalczyk, 2011].

Consequently, the most important element in the catalytic converters applied not only to automobile industry, but generally to all industries is the material for the converters carrier (metallic or ceramic). Table 1 presents samples of materials applied to industry used to make monolithic carriers. The most common used are catalytic converters with ceramic carriers. Their advantages are:

- very high specific surface,

FIG. 1 VIEW OF AUTO CATALYTIC CONVERTERS

TABLE 1 SAMPLE OF MATERIALS APPLIED IN INDUSTRY AS MONOLITHIC CARRIERS (PARYJCZAK, 2005)

Name	Chemical Components
Alumina (α, γ)	Al_2O_3
Cordierite	$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$
Mullite	$3Al_2O_3{\cdot}2SiO_2$
Magnesium spinel	$MgO{\cdot}Al_2O_3$
Cordierite-mullite	$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2\text{-}3Al_2O_3{\cdot}2SiO_2$
Mullite-aluminium titanate	$3Al_2O_3{\cdot}2SiO_2\text{-}Al_2O_3{\cdot}TiO_2$
Silica	SiO_2
Silicon carbide	SiC
Silicon nitrate	Si_2N_4
Boron carbide	B_4C
Zeolite	$Me_2O{\cdot}xAl_2O_3{\cdot}ySiO_2{\cdot}zH_2O$
Zirconium dioxide	ZrO_2
Zirconium dioxide-magnesium spinel	$ZrO_2\text{-}MgO{\cdot}Al_2O_3$
Ferrochromium	Fe-Cr-Al-(Y)
Ferritic steel	Fe
Ferritic steel-aluminium	Fe-Al
Kanthal	Fe-Cr-Al-Co

- high corrosion resistance,
- high adhesion of active substances,
- high melting temperature,
- easiness in shaping.

Generally, the catalytic carrier due to its honeycomb structure has increased surface to 4 m^2/dm^3. However, it is not sufficient for the efficient dispersion of the precious metals to the level which is necessary for effective work of catalytic converter. So, on the monolith surface, thin layer (20 – 60 μm) of aluminium oxide is spread (see Figure 2). As a result the specific surface has increased tens hundred times (10000 – 40000 m^2/dm^3). Different oxides (CeO_2, NiO or Li_2O) can be added to Al_2O_3 in the direct layer to increase properties of this layer (Online3). For example, the addition of CeO_2 increases the resistance of this layer to ageing in high temperatures.

The material predominantly used to produce monolithic ceramic carrier in automotive industry is aluminium oxide or synthetic cordierite $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$. The production of cordierite includes the following basic steps:

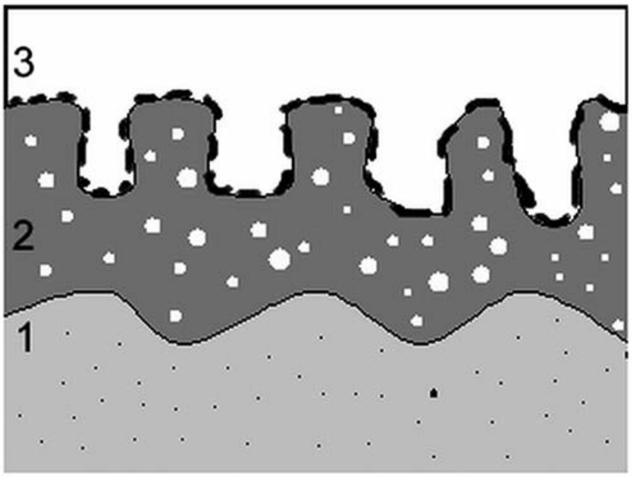


FIG. 2 LAYERS OF CATALYTIC CONVERTERS CARRIER: 1) CERAMIC MONOLITH, 2) DIRECT LAYER WITH ADDITION OF CERIUM OXIDE OR OTHER DIFFERENT ACTIVATORS, 3) CATALYTIC LAYER WITH PGM METALS (ONLINE 1)

- mixing raw oxides to obtain solid state by thermal heating,
- plasticization with water and other organic additives,
- the extrusion of obtained ceramic paste through appropriate dies,
- drying to obtain moisture without cracking,
- heating at 1450ºC to transform the raw materials into the cordierite monolithic substrate (Forzatti, 1998).

Sometimes metallic catalytic carriers are also applied, and their characteristic features are:

- easiness of heat transfer, so they are resistant to local overheating,
- small hydraulic resistances,
- high mechanic strength,
- small apparent powder density (Online 3).

The Recovery of Platinum from Used Auto Catalytic Converters

Natural resources of platinum and generally PGM metals are limited. However their demand is still growing because of their extensive use in catalysis, electronic devices, space materials, biomedical devices, etc… Therefore, low rate of production of these metals due to their small concentration in related ores, and their high production costs from ores, have made PGM metals recovery from used auto catalytic converters an interesting alternative to receiving PGM metals. Taking into consideration global reserves of PGM metals, especially platinum against their increasing demand, a revision of the consumption and utilization of these metals should be made. In addition, the emphasis should be put on the recovery and recycle of the potential waste (Shams, 2006).

During the past decade, considerable researches have been devoted to the extensive utilization of used auto catalytic converters with the Al_2O_3-based carrier. A survey of literature revealed that there are many available technologies applied to recycle the used auto catalytic converters. Most of the valuable elements in the catalytic converters have been recovered, however the carrier based on Al_2O_3 failed to have a good recovery, which also leads to another pollution (Chen, 2006).

It seems to be appropriate to describe the whole process from the beginning. The first step of recovering PGM metals and especially platinum from used auto catalytic converters is to collect and then dismantle them. After these operations catalytic converter carriers are milled and homogenized. Then chemical analysis is necessary in order to check the level of platinum and other precious metals. If the platinum level is lower than 30%, the thickening operation is applied. This stage includes processes like incineration, based on hydrometallurgy and pyrometallurgy or both together (see Figure 3).

As a result, the high level of PGM metals recovery can be obtained. In such technologies many indirect operations are used to obtain pure metal. The next stage of PGM metals recovery is to solve and separate precious metals and purify them. The purification

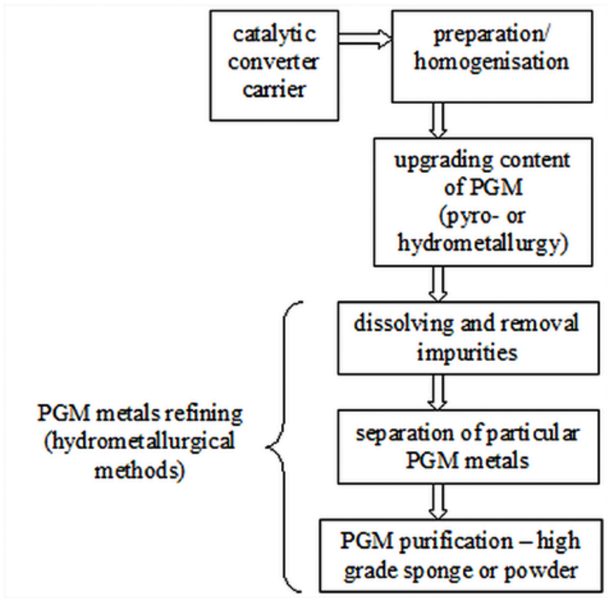


FIG. 3 STEPS OF PGM METALS RECOVERY FROM USED AUTO CATALYTIC CONVERTERS (FORNALCZYK, 2009)

allows obtaining metals with higher purity. This stage, however, requires a great amount of energy and also generates many chemical compounds hazard to the environment. Processes that can be used in PGM metals purification are: calcinations, ion exchange, solvent extraction, hydrolysis, reduction and oxidation processes, as well as precipitation. In this way it is possible to recover 95% of platinum and 80-85% of rhodium (Fornalczyk, 2009).

Melting Used Auto Catalytic Converters with Copper (Metal Collector)

Research of platinum recovery from used auto catalytic converters by means of hydro- and pyrometallurgical method was carried out. First of all, the catalytic converters were grinded and milled. Before this spectrometric analysis was done; Figures 4 and 5 presented its results. In pyrometallurgical tests catalytic converter was melted with copper (copper was treated as a metal collector) - Figure 6 presented scheme of the reactor used in this kind of tests. Copper was chosen taking into account the solubility of platinum in this metal and additionally the melting temperature of this metal. During melting process the ceramic parts of the carrier should be placed to the slag (see Figure 7).

Platinum, as its melting temperature is higher than melting temperature of metal collector, should be collected in liquid metal and create an alloy with it after solidification. Inductive furnace was used for this kind of test and what is more, the neutral atmosphere in the furnace could be kept by applying argon blow. Table 2 presents parameters of pyrometallurgical treatment of catalytic converter and the results obtained from these tests.

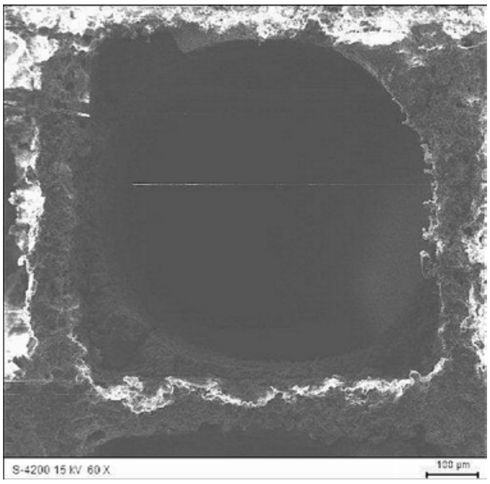


FIG. 4 VIEW OF CATALYTIC CONVERTERS CARRIER MADE BY SPECTROMETER (THERE IS ONE OF MANY CATALYTIC CARRIERS CHANNELS)

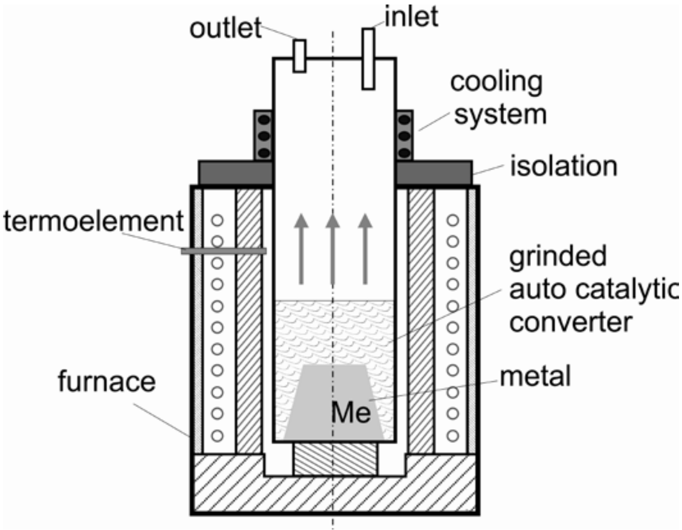


FIG. 6 SCHEME OF REACTOR USED DURING MELTING THE CATALYTIC CONVERTERS WITH COPPER

Both obtained alloy and slag were spectrometric analyzed and Figures 8 and 9 respectively present view of alloy and slag samples in microscale, whereas Figures 10 and 11 present graphhic results of such analysis.

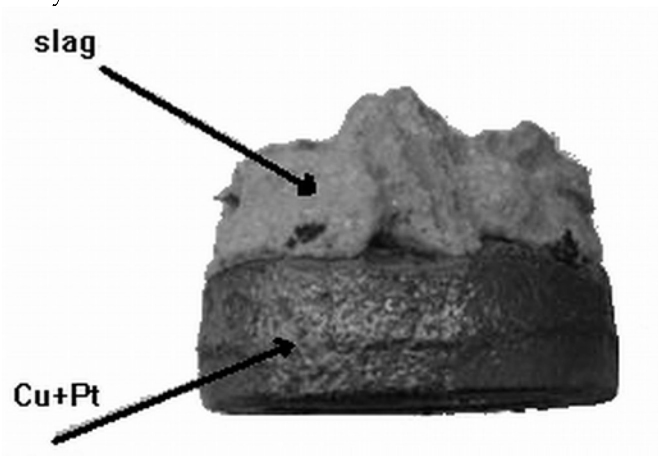
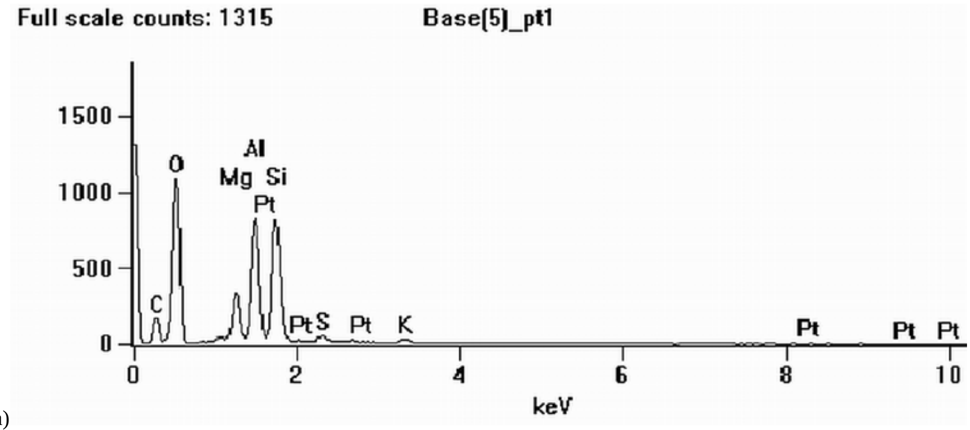


FIG. 7 SAMPLE OBTAINED AFTER PYROMETALLURGICAL TREATMENT, IT CONSISTS OF TWO LAYERS: SLAG AND COPPER WITH PLATINUM

The best results were observed for copper at the temperature 1550 ^{o}C. In that case even 95% of platinum could be recovered from catalytic converter carrier. However, higher temperature caused problems in separating slag from copper and platinum alloys. It is also possible to obtain platinum from Cu-Pt alloy – i.e. cast this alloy in the form of anode and lead electrowinning process.

Dissolving Used Auto Catalytic Converters Carriers in Aqua Regia

In hydrometallurgical tests, grinded catalytic converter was dissolved in aqua regia. Some of the test



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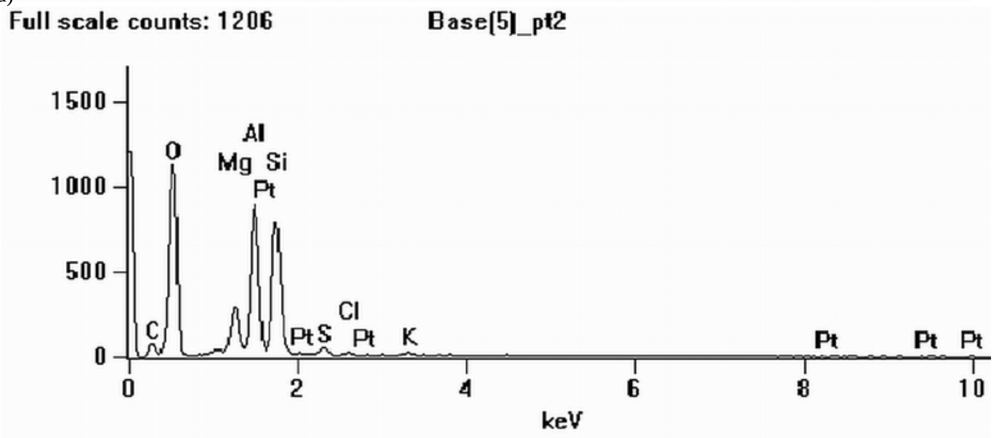

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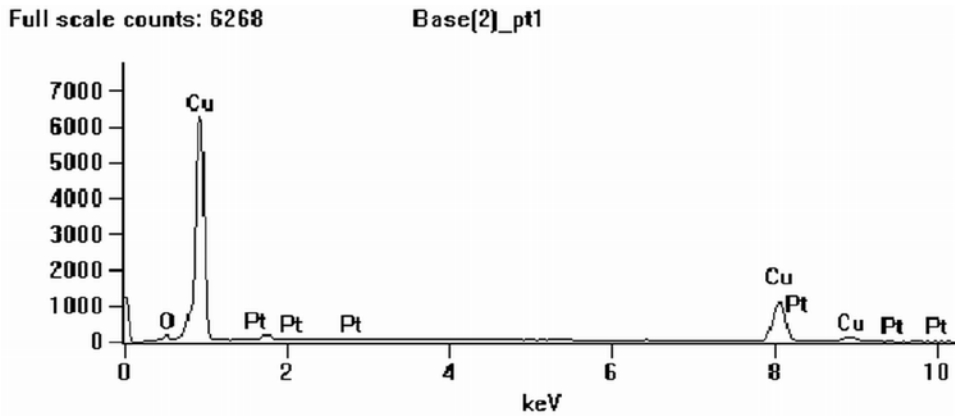
FIG. 5 RESULTS OF SPECTROMETRIC ANALYSIS MADE IN TWO DIFFERENT POINTS (A AND B) OF GIVEN SAMPLE OF CATALYTIC CONVERTER CARRIER



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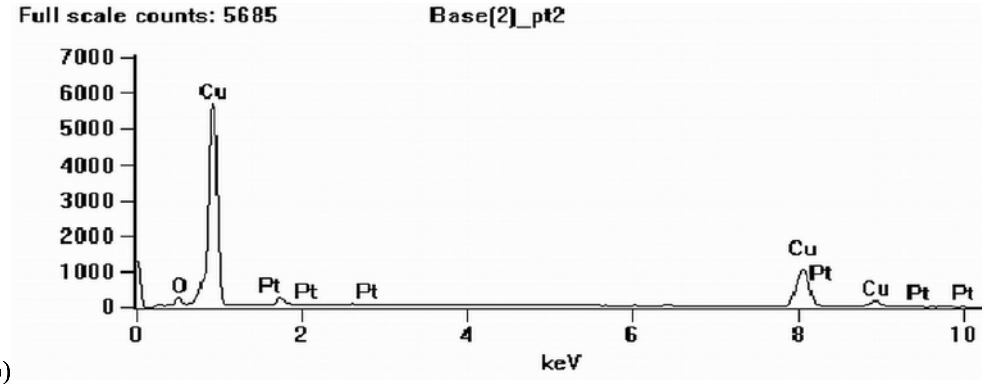

b)

FIG. 10 RESULTS OF SPECTROMETRIC ANALYSIS MADE IN TWO DIFFERENT POINTS (A AND B) OF GIVEN SAMPLE OF CU-PT ALLOY

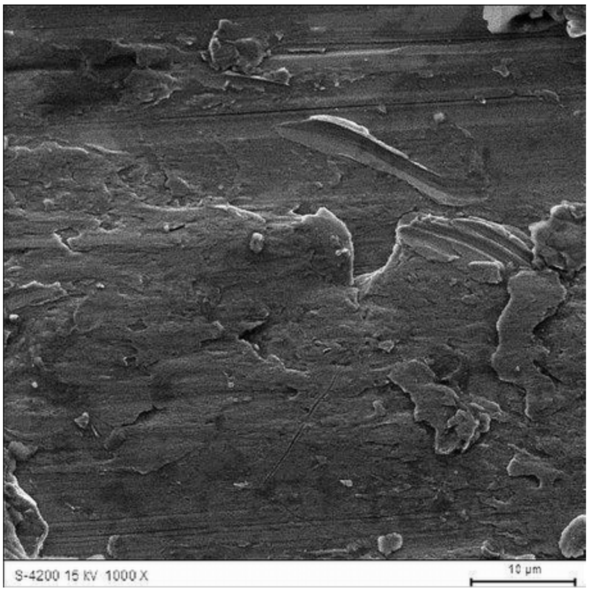

FIG. 8 VIEW OF CU-PT ALLOY MADE BY SPECTROMETER

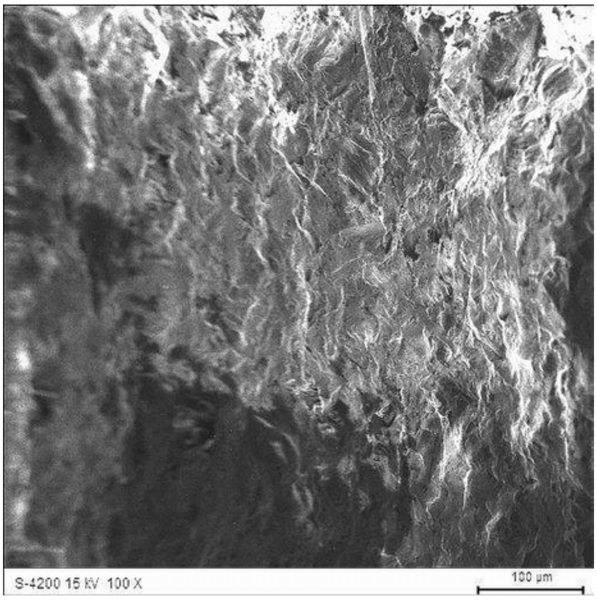

FIG. 9 VIEW OF OBTAINED SLAG MADE BY SPECTROMETER

probes were heated. Then, these probes were filtrated to separate the solution from the insoluble remains of the carrier. As a result of the filtration the solution with platinum was obtained. On the filter, parts of ceramic carrier were also obtained. Table 3 presents parameters of hydrometallurgical treatment of catalytic converter and the results obtained from these tests. Analysis of PGM metals contents in the carrier before and after melting and dissolving process in aqua regia was performed by means of atomic absorption spectroscopy.

TABLE 2 PYROMETALLURGICAL TREATMENT OF CATALYTIC CONVERTER – PROCESSING PARAMETERS AND RESULTS

Test with Copper as a Metal Collector			
Temperature °C	**Contents of Platinum**		**Recovery of Platinum %**
	After %	**Before %**	
Platinum is collected in obtained copper alloy after melting the grinded catalytic converter with the molten pure copper.			
1 550	0.196	0.036	85.2
1 700	0.196	0.050	62.8
1 550	0.218	0.045	85.6
1 700	0.218	0.055	71.3
1 550	0.258	0.075	88.3
1 700	0.258	0.052	68.8
1 550	0.281	0.080	95.2
1 700	0.281	0.060	70.1

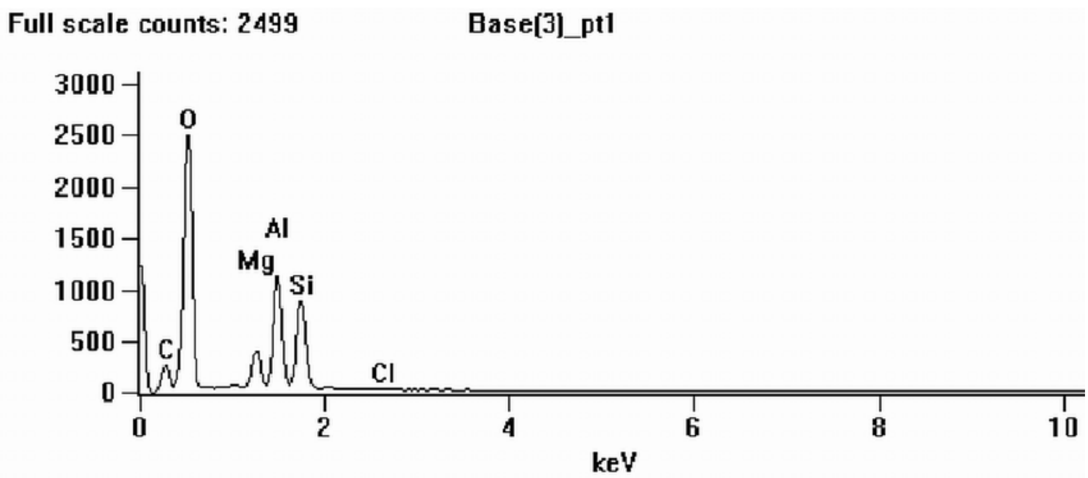

FIG. 11 RESULTS OF SPECTROMETRIC ANALYSIS OF GIVEN SAMPLE OF OBTAINED SLAG AFTER PYROMETALLURGICAL TREATMENT

TABLE 3 HYDROMETALLURGICAL TREATMENT OF CATALYTIC CONVERTER – PROCESSING PARAMETERS AND RESULTS

Test with Aqua Regia Platinum is Dissolved in the Mixture of Acid HCl and HNO_3 in the Ratio 3:1			
Time of Heating s	Contents of Platinum		Recovery of Platinum %
	After %	Before %	
0	0.230	0.154	86.6
1 200	0.230	0.163	90.1
1 500	0.230	0.191	93.3
1 800	0.230	0.207	94.2

Possibilities of Reusing the Remains of Ceramic Carrier

It is possible to recover platinum from used auto catalytic converters; however there is still one problem – how to deal with the parts of remained ceramic carriers, which is a serious problem. The temperature of Al_2O_3 melting is 2054 ^oC, and the temperature of platinum melting is lower and equals 1768 ^oC. In pyrometallurgical treatment this is advantageous because the insoluble ceramic carriers are placed to the slag and then it is easy to divide them from the metal collector (see Figure 7). In hydrometallurgical treatment ceramic carrier is obtained as a filtration remains.

In work (Chen, 2006) it is mentioned that there is possibility to obtain pure alumina from the remains after recycling used hydroprocessing catalytic converters. In some work (Marafi, 2011) alumina present in the used catalytic converters has been reclaimed as aluminium salts or fused alumina after recovering the valuable metals such as Mo, V, Ni and Co. It has been suggested to prepare α-alumina or even boehmite [AlO(OH)] from the alumina-based used hydroprocessing catalytic converters. Boehmite, a really valuable material, has a wide range of application such as: catalyst supports, coatings, polymer additives, ceramics. It is also possible to obtain γ-Al_2O_3 from ceramic carrier remains (see Figure 12). It can be used in electrolysis process to obtain pure aluminium without the production of red mud (Bayer`s method), which is harmful to the environment.

Conclusions

The amount of waste coming from automotive industry (especially used catalytic converters) has rapidly been increasing worldwide. Therefore, recovery of valuable elements such as platinum and PGM metals became an unavoidable goal to reach, which is helpful to increase the catalytic converters cost and reduce the waste to prevent the environmental pollution. It is possible also to reuse the ceramic parts of catalytic converters such as alumina, the satisfaction is full. Because there is successful research carried out on the used hydroprocessing catalytic converters, so the slag obtained during pyrometallurgical process may be treated in the same way. The further research will be conducted.

ACKNOWLEDGMENT

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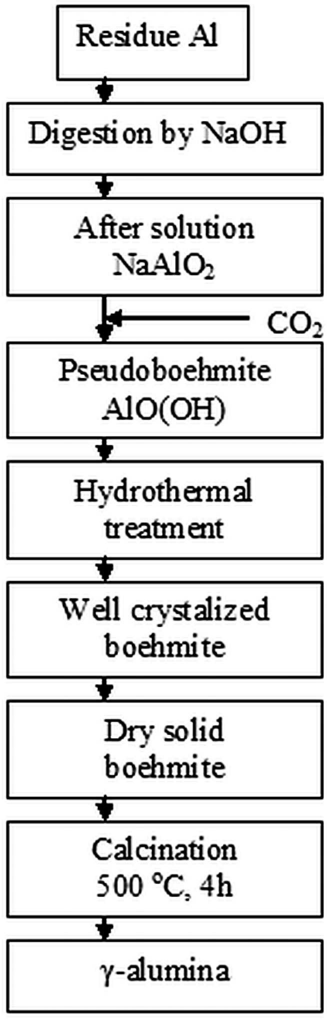

FIG. 12 FLOW DIAGRAM OF OBTAINING Γ-ALUMINA FROM USED HYDROPROCESSING CATALYTIC CONVERTERS

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